Synthesis of Novel Diarylpyrrole-2-carbaldehydes by Ring Transformations

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(Received: 4 January 2013;

Accepted: 4 October 2013)

AJC-14235

Various diarylpyrrole-2-carbaldehydes were prepared by ring transformation of arylfuran-2-carbaldehydes with anilines in the presence of an acid. The synthesized compounds were characterized through elemental analysis and spectroscopic techniques (FTIR, ¹H NMR, ¹³C NMR and mass spectra).

Key Words: Diarylpyrrole aldehydes, Ring transformation, Arylfuran-2-carbaldehydes, Meerwein arylation.

INTRODUCTION

Pyrrole is one of the most important heterocyclic compounds, having increasingly importance in medicinal chemistry and organic synthesis¹⁻⁵. Some of the recently isolated pyrrole-containing marine natural products have been found to exhibit considerable cytotoxicity and function as multi drug resistant (MDR) reversal agents. Many of these biologically active compounds have emerged as chemotherapeutic agents⁶. Due to these multiple uses and varieties of biological activities, the synthesis of this ring system has been subject of intense investigation. Several new synthetic methods and variations of classical ones reported recently either give new types of pyrroles or result in their better yields. The classical methods of constructing pyrrole ring system include mainly conjugate addition reactions⁷, transition metal-mediated reactions⁸, reductive couplings⁹, aza-Wittig reactions¹⁰ and other multistep operations¹¹ have all been performed for the synthesis of pyrroles. Despite these huge developments, the Paal-Knorr¹² reaction is still considered to be the most attractive method for the synthesis of pyrroles.

Since various *vicinal* diarylazoles/heterocycles are known to be cyclooxygenase (COX) inhibitors and some have been in clinical use *e.g.*, celecoxib (**1**) and valdecoxib (**2**)^{13,14}. These have come under criticism because of their adverse side effects^{15,16}, so there is a continuous effort in quest for finding better agents and diarylpyrroles seem to be drawing much attention of heterocyclic chemists in this regard.

Synthesis of 4,5-diarylpyrroles and their antiinflammatory activity has been reported by Wilkerson *et al.*¹⁷. Some 1,5-diarylpyrrole-1*H*-3-acetic acids (**3**), esters and 3-alkoxyethyl ethers have been synthesized as potent COX-2 inhibitors¹⁸⁻²⁰. Interestingly these authors have also reported other 1,5-diarylpyrroles as potential antimycobacterial agents^{21,22}.

Various 1,5-diarylpyrroles were reported by Hall *et al.*^{23,24} as EP1 receptor antagonists. Most of these experimental 1,5-

diarylpyrroles were prepared from appropriately substituted 1,4-diketones by the Paal-Knorr method¹². 2,5-Dialkoxytetrahydrofurans are “masked” or cyclic acetals of 1,4-dialdehydes which either under acid catalysis²⁵ or under microwave irradiation in the presence of iodine²⁶ react with aromatic amines affording N-arylpyrroles. A ring transformation of furan-2-carbaldehyde to 1-arylpyrrole-2-carbaldehyde takes place in the presence of an arylamine and an acid catalyst^{27,28}. This general reaction had provided us N-arylpyrrole-2-carbaldehydes in good yields and has encouraged us to attempt these ring transformations with 5-arylfuran-2-carbaldehydes. The reactions were successful and here we would like to present our findings. It is to be noted that the resultant products carrying a carbaldehyde function opens up various possibilities of preparation of diverse derivatives of 1,5-diarylpyrroles.

EXPERIMENTAL

All reagents and solvents were used as obtained from the supplier or recrystallized or redistilled as were found necessary. Thin layer chromatography was performed using aluminium sheets (Merck) coated with silica gel 60 F₂₅₄. IR spectra were recorded by using an IR Perkin-Elmer spectrum 1 FTIR spectrophotometer and peaks are reported max (neat)/cm⁻¹ which refer to the min wave numbers. Proton magnetic resonance spectra were recorded in deuteriochloroform with Bruker AM 300 spectrometers (Rheinstetten–Forchheim, Germany) operating at 300 MHz, respectively. The ¹³C NMR spectra were recorded in Deuteriochloroform with Bruker AM 100 spectrometer operating at 100 MHz. Tetramethylsilane was used as an internal standard. Elemental analysis for C, H and N were recorded with Perkin-Elmer 2400 Series II CHN Analyzer. Melting points were recorded on a Gallenkamp apparatus and are uncorrected.

General procedure for the synthesis of 5-arylfuran-2-carbaldehydes: Substituted aniline (0.01 mol) is dissolved in a mixture of conc. hydrochloric acid and 20 mL of water under stirring and cooled in an ice bath at -5 °C. A solution of sodium nitrite (2 g in 10 mL of water) is added portion wise, keeping the temperature below 7-8 °C. The reaction mixture is left for 1 h for the completion of diazotization, filtered with the help of glass wool (in case there is any turbidity observed). The filtered diazonium solution is added drop wise to a solution of furfural (2 mL in 10 mL of acetone and water) followed by a solution of copper chloride (2 g in 10 mL of water). The temperature is raised to 30 °C by heating (if necessary) and stirred for 4-6 h then left for 24 h at room temperature. Precipitates obtained are filtered, dried and recrystallized from ethanol.

Following 5-arylfuran-2-carbaldehydes are prepared in this manner:

5-(4'-Nitrophenyl)furan-2-carbaldehyde (4): Yellow crystals, m.p. 196 °C (EtOH) (m.p. 192 °C (EtOH))³³.

5-(4'-Chlorophenyl)furan-2-carbaldehyde (5): Light yellow crystals, m.p. 118 °C (EtOH) (m.p. 118 °C (EtOH))³³.

5-(4'-Bromophenyl)furan-2-carbaldehyde (6): Off white crystals, m.p. 150 °C (EtOH) (m.p. 150 °C (EtOH))³³.

4-(5'-Formylfuran-2'-yl)benzoic acid (7): Light brown crystals, m.p. 296 °C (EtOH). FTIR (KBr, $\nu_{\max}$, cm⁻¹): 2360.14 (aromatic ring) 1672.39 (C=O acid) 2968.44 (-OH acid)

1610.63 (C=O aldehyde) ¹H NMR spectrum (CDCl₃, 300 MHz), δ ppm (*J*, Hz): 9.567 (1H, s, Ar-CHO); 7.797 (1H, d, *J* = 6.40, Ar-H), 7.877 (1H, d, *J* = 6.00, Ar-H), 7.288 (1H, d, *J* = 6.30, Ar-H), 8.021 (1H, d, *J* = 6.50, Ar-H), 6.893 (1H, d, *J* = 2.40, furyl proton), 7.238 (1H, d, *J* = 2.40, furyl proton) ¹³C NMR spectrum (CDCl₃, 75 MHz) δ ppm: 178.51 (Ar-CHO), 165.96 (-COOH) 155.43, 153.90, 132.46, 127.65, 123.87, 122.43, 122.09, 117.78, 109.89 (Ar-C) mass spectrum (EI, 70 eV, (*I*_{rel} %): 216 [M⁺] (100), 199 [M⁺-OH] (11) *m/z* 170 [M⁺-COOH] (7), *m/z* 76 [Ph] (4), found (%) C 66.71; H 3.76; C₁₂H₈O₄ (216), calcd. (%) : C 66.66; H 3.70.

General method for the ring transformation reaction of 5-arylfuran-2-carbaldehydes: Equimolar quantities (0.01 mole) of a 5-arylfuran-2-carbaldehyde and aniline are refluxed in 20 mL ethanol for 6 h in the presence of conc. hydrochloric acid (0.5 mL) as a catalyst and then poured the reaction mixture over crushed ice, the precipitates are filtered, dried and recrystallized from ethanol.

5-(4'-Nitrophenyl)-1-phenyl-1H-pyrrole-2-carbaldehyde (8): Reddish crystals, m.p. 102 °C (EtOH) FTIR KBr, $\nu_{\max}$, cm⁻¹): 1599.16 (C=O aldehyde), 1538.50 and 1333.39 (asym and sym -NO₂), ¹H NMR spectrum (CDCl₃, 300 MHz), δ ppm (*J*, Hz): 9.41 (s, 1H, CHO), 7.939-7.008 (m, 9H, Ar-H), 7.001 (d, 1H, pyrrole-H *J* = 3.10 Hz), 6.678 (d, 1H, pyrrole-H, *J* = 3.10 Hz) ¹³C NMR spectrum (CDCl₃, 75 MHz) δ ppm: 175.65 (C=O aldehyde), 145.08, 131.93, 129.75, 129.54, 124.27, 123.66, 123.56, 115.46, 115.16, 110.87, 109.89 (Ar-C) mass spectrum (EI, 70 eV, (*I*_{rel} %): *m/z* 293 [M⁺] (20), 263 [M⁺-CHO] (10), 93 [M⁺-PhNO₂-Ph] (13) found (%) C 69.54; H 4.22; N 9.89 C₁₇H₁₂N₂O₃ (293) calcd. (%) C 69.86; H 4.10; N 9.59.

5-(4'-Nitrophenyl)-1-(4''-nitrophenyl)-1H-pyrrole-2-carbaldehyde (9): Dark red crystals, m.p. 124 °C (EtOH) FTIR KBr, $\nu_{\max}$, cm⁻¹): 2362.53 (aromatic ring) 1628.46 (C=O aldehyde), 1587.22 and 1296.40 (asym and sym -NO₂) ¹H NMR spectrum (CDCl₃, 300 MHz), δ ppm (*J*, Hz): 9.71 (s, 1H, CHO), 8.306-7.026 (m, 8H, Ar-H), 7.017 (d, 1H, pyrrole-H *J* = 3.45 Hz), 6.594 (d, 1H, pyrrole-H, *J* = 3.45 Hz) ¹³C NMR spectrum (CDCl₃, 75 MHz) δ ppm: 177.54 (C=O aldehyde), 134.58, 126.33, 125.78, 125.57, 125.21, 124.43, 123.86, 123.63, 122.63, 121.48, 113.41, 109.75 (Ar-C) Mass spectrum (EI, 70 eV, (*I*_{rel} %): *m/z* 337 [M⁺] (11), 215 [M⁺-PhNO₂] (100), 187 [M⁺-PhNO₂-CHO] (47) found (%) C 60.34; H 3.05; N 12.26 C₁₇H₁₁N₃O₅ (337) calcd. (%) C 60.53; H 3.26; N 12.46.

5-(4'-Nitrophenyl)-1-(4''-chlorophenyl)-1H-pyrrole-2-carbaldehyde (10): Brown crystals, m.p. 124 °C (EtOH) FTIR KBr, $\nu_{\max}$, cm⁻¹): 2360.42 (aromatic ring) 1684.99 cm⁻¹ (C=O aldehyde), 1042.43 (C-Cl bond), 1600.22 and 1358.09 (asym -NO₂), ¹H NMR spectrum (CDCl₃, 300 MHz), δ ppm (*J*, Hz): 9.718 (s, 1H, CHO), 8.312-7.341 (m, 8H, Ar-H), 7.029 (d, 1H, pyrrole-H *J* = 2.80 Hz), 7.017 (d, 1H, pyrrole-H, *J* = 2.80 Hz) ¹³C NMR spectrum (CDCl₃, 75 MHz) δ ppm: 177.55 (C=O aldehyde), 142.55, 131.78, 129.48, 125.76, 125.23, 124.42, 122.68, 122.31, 110.62 (Ar-C) mass spectrum (EI, 70 eV, (*I*_{rel} %): *m/z* 28 [M⁺+2], 326 [M⁺] (7.1), 215 [M⁺-PhCl] (100) Found (%) C 62.32; H 3.13; N 8.44 C₁₇H₁₁ClN₂O₃ (326) calcd. (%) C 62.57; H 3.37; N 8.58.

5-(4'-Nitrophenyl)-1-(4''-bromophenyl)-1H-pyrrole-2-carbaldehyde (11): Yellow crystals. m.p. 232 °C (EtOH). FTIR KBr, $\nu_{\max}$, cm⁻¹): 1655.84 (C=O aldehyde), 1594.41 and

1361.51 (-NO₂), 2365.43 (aromatic ring), 1037.49 cm⁻¹ (C-Br bond) ¹H NMR spectrum (CDCl₃, 300MHz), δ ppm(*J*, Hz): 9.636 (s, 1H, CHO), 8.360-7.618 (m, 8H, Ar-H), 7.019 (d, 1H, pyrrole-H, *J* = 3.15 Hz), 6.655 (d, 1H, pyrrole-H, *J* = 3.15 Hz) ¹³C NMR spectrum (CDCl₃, 75 MHz) δ ppm: 177.45 (C=O aldehyde), 142.66, 132.34, 132.23, 131.83, 131.60, 131.11, 130.93, 126.71, 125.23, 113.91, 108.06 (Ar-C) mass spectrum (EI, 70 eV, (*I*_{rel} %): *m/z* 372 [M⁺+2] (100), 370 [M⁺] (91) found (%) C 54.98; H 2.76; N 7.44 C₁₇H₁₁BrN₂O₃(370) calcd. (%) C 55.13; H 2.97; N 7.56.

4-(5'-Formyl-1-(4''-nitrophenyl)-1H-pyrrol-1-yl)benzoic acid (12): Brown crystals, m.p. 150 °C (EtOH) FTIR (KBr, *v*_{max}, cm⁻¹): 3263.72 (aromatic ring), 1715.12 (C=O acid), 1686.17 (C=O aldehyde), 1599.94 and 1341.94 (Asym and sym -NO₂), 3114.28 (-OH acid) ¹H NMR spectrum (CDCl₃, 300 MHz), δ ppm (*J*, Hz): 9.721 (s, 1H, CHO), 8.317-7.342 (m, 8H, Ar-H), 7.029 (d, 1H, pyrrole-H, *J* = 2.85 Hz), 7.017 (d, 1H, pyrrole-H, *J* = 2.85 Hz), ¹³C NMR spectrum (CDCl₃, 75 MHz) δ ppm: 178.89 (C=O aldehyde), 140.36, 131.58, 130.87, 130.21, 128.90, 127.60, 125.03, 113.83, 109.31, 106.55 (Ar-C) Mass spectrum (EI, 70 eV, (*I*_{rel} %): *m/z* 336 [M⁺] (78), 306 [M⁺-CHO] (66), 289 [M⁺-NO₂] (32) found (%) C 64.21; H 3.46; N 8.21 C₁₈H₁₂N₂O₅ (336) calcd. (%) C 64.28; H 3.57; N 8.33.

5-(4'-Chlorophenyl)-1-phenyl-1H-pyrrole-2-carbaldehyde (13): Yellow crystals, m.p. 82 °C (EtOH) FTIR (KBr, *v*_{max}, cm⁻¹): 1614.87 (C=O aldehyde), 1092.01 (C-Br bond), ¹H NMR spectrum (CDCl₃, 300MHz), δ ppm(*J*, Hz): 9.610 (s, 1H, CHO), 7.707-7.189 (m, 8H, Ar-H), 7.033 (d, 1H, pyrrole-H, *J* = 3.50 Hz), 6.514 (d, 1H, pyrrole-H, *J* = 3.50 Hz) ¹³C NMR spectrum (CDCl₃, 75 MHz) δ ppm: 178.90 (C=O aldehyde), 144.87, 132.43, 129.74, 129.61, 128.70, 125.95, 125.64, 125.39, 124.73, 123.13, 121.04, 110.08, 106.04 (Ar-C) mass spectrum (EI, 70 eV, (*I*_{rel} %): *m/z* 284 [M⁺+2], 282 [M⁺] (40), 254 [M⁺-CHO] (5) found (%) C 72.25; H 4.52; N 4.76 C₁₇H₁₂ClNO (281) calcd. (%) C 72.59; H 4.27; N 4.98.

5-(4'-Chlorophenyl)-1-(4''-nitrophenyl)-1H-pyrrole-2-carbaldehyde (14): Light brown crystals m.p. 165 °C (EtOH) FTIR (KBr, *v*_{max}, cm⁻¹): 1628.38 (C=O aldehyde), 1584.86 and 1328.36 (asym and sym -NO₂), 1094.51 (C-Cl bond), ¹H NMR spectrum (CDCl₃, 300 MHz), δ ppm (*J*, Hz): 9.638 (s, 1H, CHO), 8.072-7.295 (m, 8H, Ar-H), 7.322 (d, 1H, pyrrole-H, *J* = 3.20 Hz), 6.821 (d, 1H, pyrrole-H, *J* = 3.20 Hz) ¹³C NMR spectrum (CDCl₃, 75 MHz) δ ppm: 177.22 (C=O aldehyde), 152.37, 149.29, 129.27, 128.95, 126.52, 126.33, 125.11, 124.90, 121.45, 113.37, 108.50, 107.97 (Ar-C) mass spectrum (EI, 70 eV, (*I*_{rel} %): *m/z* 328 [M⁺+2], 326 [M⁺] (72), 205 [M⁺-PhNO₂] (100) found (%) C 62.13; H 3.11; N 8.64 C₁₇H₁₁ClN₂O₃ (326) calcd. (%) C 62.57; H 3.37; N 8.58.

5-(4'-Chlorophenyl)-1-(4''-chlorophenyl)-1H-pyrrole-2-carbaldehyde (15): Dark red crystals, m.p. 196 °C (EtOH); FTIR (KBr, *v*_{max}, cm⁻¹): 1658.80 (C=O aldehyde), 2563.01 (aromatic ring), 1092.17 (C-Cl bond) ¹H NMR spectrum (CDCl₃, 300 MHz), δ ppm(*J*, Hz): 9.639 (s, 1H, CHO), 7.754-7.293 (m, 8H, Ar-H), 7.220 (d, 1H, pyrrole-H, *J* = 3.50 Hz), 6.808 (d, 1H, pyrrole-H, *J* = 3.50 Hz). ¹³C NMR spectrum (CDCl₃, 75 MHz) δ ppm: 177.21 (C=O aldehyde), 135.70, 129.29, 129.15, 128.78, 127.51, 126.53, 125.65, 123.16, 118.45, 108.61, 107.97 (Ar-C) mass spectrum (EI, 70 eV,

(*I*_{rel} %): *m/z* 317 [M⁺+2], 315 [M⁺] (100), 204 [M⁺-PhCl] (12), 111 [PhCl] (45) 75 [Ph] (27), 139 [PhCl] (69), 280 [M⁺-Cl] (11) found (%) C 64.31; H 3.18; N 4.32, C₁₇H₁₁Cl₂NO (315) calcd. (%) C 64.55; H 3.48; N 4.43

5-(4'-Chlorophenyl)-1-(4''-bromophenyl)-1H-pyrrole-2-carbaldehyde (16): Brown crystals, m.p. 98 °C (EtOH) FTIR (KBr, *v*_{max}, cm⁻¹): 1677.94 (C=O aldehyde), 2322.89 (aromatic ring), 1094.65 (C-Cl bond), 1040.37 (C-Br bond), ¹H NMR spectrum (CDCl₃, 300 MHz), δ ppm (*J*, Hz): 9.636 (s, 1H, CHO), 7.750-7.292 (m, 8H, Ar-H), 6.818 (d, 1H, pyrrole-H, *J* = 7.50 Hz), 6.204 (d, 1H, pyrrole-H, *J* = 2.80 Hz) ¹³C NMR spectrum (CDCl₃, 75 MHz) δ ppm: 177.18 (C=O aldehydes), 158.19, 152.20, 135.67, 129.26, 128.94, 127.49, 126.50, 124.94, 123.27, 107.95 (Ar-C) mass spectrum (EI, 70 eV, (*I*_{rel} %): *m/z* 361 [M⁺+2] (100), 359 [M⁺] (72), 111 [PhCl] (43) found (%) C 56.91; H 3.10; N 3.56 C₁₇H₁₁BrClNO (359) calcd. (%) C 56.82; H 3.06; N 3.89.

4-(2''-Formyl-5-(4'-chlorophenyl)-1H-pyrrol-1-yl)benzoic acid (17): Light yellow crystals, m.p. 212 °C (EtOH) FTIR (KBr, *v*_{max}, cm⁻¹): 2341.29 (aromatic ring) 1717.11 (C=O acid), 1659.90 (C=O aldehyde) 3115.21 (-OH acid), 1094.88 (C-Cl bond), ¹H NMR spectrum (CDCl₃, 300MHz), δ ppm(*J*, Hz): 9.639 (s, 1H, CHO), 7.755-7.293 (m, 8H, Ar-H), 7.221 (d, 1H, pyrrole-H, *J* = 3.20 Hz), 6.808 (d, 1H, pyrrole-H, *J* = 3.20 Hz), 11.559 (COOH). ¹³C NMR spectrum (CDCl₃, 75 MHz) δ ppm: 177.45 (C=O aldehyde), 147.59, 134.92, 133.56, 130.24, 129.63, 129.22, 125.05, 124.44, 123.12, 121.28, 110.72, 108.01 (Ar-C) mass spectrum (EI, 70 eV, (*I*_{rel} %): *m/z* 327 [M⁺+2], 325 [M⁺] (53), 279 [M⁺-COOH] (33), 217 [M⁺-PhCOOH] (33) Found 5 C 66.08; H 3.59; N 3.98 C₁₈H₁₂ClNO₃ (325) calcd. (%) C 66.46; H 3.69; N 4.30.

5-(4'-Bromophenyl)-1-phenyl-1H-pyrrole-2-carbaldehyde (18): Red crystals, m.p. 122 °C (EtOH) FTIR (KBr, *v*_{max}, cm⁻¹): 2341.84 (aromatic ring) 1661.86 (C=O aldehyde) ¹H NMR spectrum (CDCl₃, 300 MHz), δ ppm(*J*, Hz): 9.635 (s, 1H, CHO), 8.282 (d, 2H, Ar-H), 7.680 (d, 2H, Ar-H, *J* = 4.50 Hz) 7.572 (d, 1H, Ar-H, *J* = 4.50 Hz), 7.441 (d, 1H, Ar-H), 7.299 (d, 1H, 7.220 (d, pyrrole-H, *J* = 2.75 Hz), 6.827 (d, pyrrole-H, *J* = 2.75 Hz) ¹³C NMR spectrum (CDCl₃, 75 MHz) δ ppm: 177.23 (C=O aldehyde), 166.39 (COOH), 165.91 (C=O ester), 158.22, 152.18, 132.21, 131.97, 131.72, 129.60, 127.89, 126.18, 125.09, 123.94, 123.34, 121.18, 108.04 (Ar-C) mass spectrum (EI, 70 eV, (*I*_{rel} %): *m/z* 327 [M⁺+2], 325 [M⁺] (12), 250 [M⁺-Ph] (100) found (%) vC 62.98; H 3.43; N 4.61 C₁₇H₁₂BrNO (325) calcd. (%) C 62.76; H 3.69; N 4.30.

5-(4'-Bromophenyl)-1-(4''-nitrophenyl)-1H-pyrrole-2-carbaldehyde (19): Brown crystals, m.p. 128 °C (EtOH) FTIR (KBr, *v*_{max}, cm⁻¹): 2363.80 (aromatic ring) 1628.71 (C=O aldehyde), 1586.45 and 1298.23 (asym and sym -NO₂), 1033.65 (C-Br bond), ¹H NMR spectrum (CDCl₃, 300 MHz), δ ppm (*J*, Hz) : 9.642 (s, 1H, CHO), 7.564 (d, 2H, Ar-H), 7.521 (d, 2H, Ar-H), 7.492 (d, 1H, Ar-H), 7.304 (d, 1H, Ar-H), 6.721 (d, pyrrole-H, *J* = 3.50 Hz), 6.622 (d, pyrrole-H, *J* = 3.50 Hz) ¹³C NMR spectrum (CDCl₃, 75 MHz) δ ppm: 177.47 (C=O aldehyde), 149.38, 130.24, 126.33, 125.12, 125.06, 124.70, 123.06, 121.47, 109.36 (Ar-C) mass spectrum (EI, 70 eV, (*I*_{rel} %): *m/z* 372 [M⁺+2], 370 [M⁺] (100), 342 [M⁺-CHO] (50), 325 [M⁺-NO₂] (25), 245 [M⁺-PhNO₂] (22), 217 [M⁺-PhBr] (11)

found (%) C 54.90; H 2.70; N 7.21 $C_{17}H_{11}BrN_2O_3$ (370) calcd. (%) C 55.13; H 2.97; N 7.56.

5-(4'-Bromophenyl)-1-(4''-chlorophenyl)-1H-pyrrole-2-carbaldehyde (20): Dark brown crystals, m.p. 182 °C (EtOH) FTIR (KBr, ν_{max} , cm^{-1}): 2360.76 (aromatic ring) 1660.03 (C=O aldehyde) 1073.87 (C-Cl bond), 1041.48 (C-Br bond), 1H NMR spectrum ($CDCl_3$, 300 MHz), δ ppm (J , Hz): 9.639 (s, 1H, CHO), 7.687 (d, 2H, Ar-H), 7.651 (d, 2H, Ar-H) 7.578 (d, 1H, Ar-H), 7.304 (d, 1H, Ar-H), 6.833 (d, pyrrole-H, J = 3.15 Hz), 6.821 (d, pyrrole-H, J = 3.15 Hz). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) δ ppm: 177.25 (C=O aldehyde), 142.33, 133.97, 132.22, 126.71, 125.41, 123.56, 121.09, 108.06 (Ar-C) mass spectrum (EI, 70 eV, (I_{rel} %): m/z 361 [M^+ +2] (100), 359 [M^+] (75), 326 [M^+ +2-Cl] (5), 280 [M^+ -Br] (5.5), 155 [PhBr] (5.3), 250 [M^+ +2-PhCl] (40) Found (%) C 56.97; H 2.91; N 3.65 $C_{17}H_{11}BrClNO$ (359) calcd. (%) C 56.82; H 3.06; N 3.90.

5-(4'-Bromophenyl)-1-(4''-bromophenyl)-1H-pyrrole-2-carbaldehyde (21): Reddish crystals m.p. 142 °C (EtOH) FTIR (KBr, ν_{max} , cm^{-1}): 2341.15 (aromatic ring) 1679.42 (C=O aldehyde), 1041.68 (C-Br bond), 1H NMR spectrum ($CDCl_3$, 300MHz), δ ppm (J , Hz): 9.638 (s, 1H, CHO), 7.686 (d, 2H, Ar-H), 7.658 (d, 2H, Ar-H), 7.577 (d, 1H, Ar-H, J = 7.80 Hz, J = 8.90 Hz), 7.303 (d, 1H, Ar-H, J = 9.80 Hz, J = 8.60 Hz), 6.832 (d, pyrrole-H, J = 2.90 Hz), 6.820 (d, pyrrole-H, J = 2.90 Hz) ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) δ ppm: 177.24 (C=O aldehyde), 158.24, 142.89, 132.24, 127.93, 126.72, 123.96, 108.07 (Ar-C) mass spectrum (EI, 70 eV, (I_{rel} %): m/z 405 [M^+] (57), 326 [M^+ -Br] (4), 250 [M^+ -PhBr] (100), 155 [PhBr] (11), 222 [M^+ -PhBr-CHO] (11) found (%) C 50.34; H 2.65; N 3.21 $C_{17}H_{11}Br_2NO$ (403) calcd. (%) C 50.62; H 2.73; N 3.47.

4-(2'-Formyl-5-(4'-bromophenyl)-1H-pyrrol-1-yl) benzoic acid (22): Yellow crystals, m.p. 192 °C (EtOH) FTIR (KBr, ν_{max} , cm^{-1}): 2363.82 (aromatic ring) 1681.83 (C=O aldehyde), 1041.51 (C-Br bond). NMR spectrum ($CDCl_3$, 300 MHz), δ ppm (J , Hz): 9.640 (s, 1H, CHO), 7.893 (d, 2H, Ar-H), 7.688 (d, 2H, Ar-H, J = 8.60 Hz), 7.578 (d, 1H, Ar-H, J = 8.6 Hz), 7.304 (d, 1H, Ar-H, J = 8.50 Hz), 6.833 (d, pyrrole-H, J = 3.30 Hz) 6.652 (d, pyrrole-H, J = 3.30 Hz), 11.583 (COOH) ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) δ ppm: 177.29 (C=O aldehyde), 158.24 (COOH) 148.72, 132.39, 132.23, 132.08, 131.90, 127.92, 126.71, 125.87, 125.23, 123.96, 120.96, 111.89, 108.05 (Ar-C) mass spectrum (EI, 70 eV, (I_{rel} %): m/z 371 [M^+ +2], 369 [M^+] (49), 290 [M^+ -Br] (6), 214 [M^+ -PhBr] (4), 155 [PhBr] (8) Found (%) C 61.05; H 3.56; N 6.71 $C_{18}H_{12}BrNO_3$ (369) calcd. (%) C 60.81; H 3.22; N 6.45.

4-(5'-Formyl-1-phenyl-1H-pyrrol-2-yl) benzoic acid (23): Yellow crystals, m.p. 136 °C (EtOH) FTIR (KBr, ν_{max} , cm^{-1}): 2341.82 (aromatic ring), 1690.43 (C=O acid), 1678.61 (C=O aldehyde), 1H NMR spectrum ($CDCl_3$, 300MHz), δ ppm (J , Hz): 9.637 (s, 1H, CHO), 8.030-7.420 (m, 8H, Ar-H), 6.978 (d, 1H, pyrrole-H, J = 3.15 Hz), 6.658 (d, 1H, pyrrole-H, J = 3.15 Hz) ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) δ ppm: 178.35 (C=O aldehyde) 155.67, 131.58, 130.26, 130.21, 128.91, 125.07, 109.34 (Ar-C) Mass spectrum (EI, 70 eV, (I_{rel} %): m/z 290 [M^+] (7), 77 [Ph] (38), 93 [PyrroleCHO] (100) found (%) C 74.01; H 4.35; N 5.05 $C_{18}H_{13}NO_3$ (291) calcd. C 74.22; H 4.46; N 4.81.

4-(5'-Formyl-1-(4''-nitrophenyl)-1H-pyrrol-2-yl) benzoic acid (24): Red colour crystals, m.p. 182 °C, (EtOH) FTIR (KBr, ν_{max} , cm^{-1}): 1679.78 (C=O acid), 1627.13 (C=O aldehyde) 1586.60 and 1331.93 (asym and sym -NO₂), 3365.23 (-OH acid), 1H NMR spectrum ($CDCl_3$, 300MHz), δ ppm (J , Hz): 9.692 (s, 1H, CHO), 8.069-8.039 (m, 8H, Ar-H), 6.620 (d, 1H, pyrrole-H, J = 2.85 Hz), 6.590 (d, 1H, pyrrole-H, J = 2.85 Hz), ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) δ ppm: 177.45 (C=O aldehyde), 166.78, 147.96, 142.63, 132.86, 130.82, 130.26, 130.22, 125.07, 125.03, 122.91, 109.35 (Ar-C) mass spectrum (EI, 70 eV, (I_{rel} %): m/z 336 [M^+] (100), 306 [M^+ -CHO] (26), 289 [M^+ -NO₂] (19), 216 [M^+ -PhCOOH] (6) found (%) C 64.34; H 3.36; N 8.57 $C_{18}H_{12}N_2O_5$ (336) calcd. (%) C 64.28; H 3.57; N 8.33.

4-(5'-Formyl-1-(4''-chlorophenyl)-1H-pyrrol-2-yl) benzoic acid (25): Brown crystals, m.p. 250 °C (EtOH) FTIR (KBr, ν_{max} , cm^{-1}): 2348.57 (aromatic ring) 1676.17 (C=O aldehyde) 1045.88 (C-Cl bond), 2979.83 (-OH acid), 1H NMR spectrum ($CDCl_3$, 300 MHz), δ ppm (J , Hz): 9.683 (s, 1H, CHO), 8.301-7.331 (m, 8H, Ar-H), 6.960 (d, 1H, pyrrole-H, J = 3.50 Hz), 6.934 (d, 1H, pyrrole-H, J = 3.50 Hz), 11.945 (s, COOH) ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) δ ppm: 178.79 (C=O aldehyde), 162.56, 147.95, 142.62, 132.86, 130.82, 130.26, 130.22, 125.07, 122.92, 118.76, 110.90 (Ar-C) Mass spectrum (EI, 70 eV, (I_{rel} %): m/z 371 [M^+ +2], 325 [M^+] (4), 216 [M^+ -PhCOOH] (100) found (%) C 66.24; H 3.78; N 4.11 $C_{18}H_{12}ClNO_3$ (325) calcd. (%) C 66.46; H 3.69; N 4.30.

4-(5'-Formyl-1-(4''-bromophenyl)-1H-pyrrol-2-yl) benzoic acid (26): Brown crystals, m.p. 262 °C (EtOH) FTIR (KBr, ν_{max} , cm^{-1}): 2983.52 (-OH) 1609.50 (C=O aldehyde), 1673.98 (C=O carboxylic acid) 2363.93 (aromatic ring), 1045.95 (C-Br bond), 2829.98 cm^{-1} (C-H stretch of aldehyde), 1H NMR spectrum ($CDCl_3$, 300MHz), δ ppm (J , Hz): 9.780 (s, 1H, CHO), 8.406-7.569 (m, 8H, Ar-H), 6.965 (d, 1H, pyrrole-H, J = 2.95 Hz), 6.732 (d, 1H, pyrrole-H, J = 2.95 Hz), 11.675 (s, COOH) ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) δ ppm: 178.45 (C=O aldehyde), 165.67 (COOH), 141.67, 130.22, 125.03, 123.11, 122.09, 109.30 (Ar-C) mass spectrum (EI, 70 eV, (I_{rel} %): m/z 371 [M^+ +2], 369 [M^+] (12), 216 [M^+ -PhCOOH] (50) found (%) C 58.18; H 3.39; N 3.61 $C_{18}H_{12}BrNO_3$ (369) calcd. (%) C 58.53; H 3.25; N 3.79.

4-(5'-Formyl-1-(4''-carboxyphenyl)-1H-pyrrol-2-yl) benzoic acid (27): Light yellow crystals, m.p. 202 °C (EtOH) FTIR (KBr, ν_{max} , cm^{-1}): 2341.42 (aromatic ring) 1680.53 (C=O acid), 1593.20 (C=O aldehyde) 2980.73 (-OH acid), 1H NMR spectrum ($CDCl_3$, 300MHz), δ ppm (J , Hz): 9.636 (s, 1H, CHO), 8.314-7.425 (m, 8H, Ar-H), 6.812 (d, 1H, pyrrole-H, J = 5.50 Hz), 6.742 (d, 1H, pyrrole-H, J = 3.50 Hz), 11.410 (s, COOH) ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) δ ppm: 179.85 (C=O aldehyde), 166.39 (COOH), 148.76, 142.35, 133.78, 132.89, 131.09, 129.65, 123.64, 122.70, 119.62, 110.69 (Ar-C) mass spectrum (EI, 70 eV, (I_{rel} %): m/z 336 [M^+] (4), 304 [M^+ -CHO] (50) found (%) C 68.01; H 3.72; N 4.11 $C_{19}H_{13}NO_5$ (335) calcd. (%) C 68.05; H 3.88; N 4.17.

RESULTS AND DISCUSSION

Various arylfurfurals (**4-7**) were prepared in 40-70 % yield by catalytic arylation of furfural with arenediazonium salts according to Meerwein method²⁹. These were treated with

appropriate anilines at reflux in ethanol in the presence of a catalytic amount of hydrochloric acid to provide, in good yields, the respective 1,5-diarylpyrrole-2-carbaldehydes (**8-27**) by a ring transformation reaction (**Scheme-I**). The procedure followed the one reported for the preparation of 1-arylpyrrole-2-carbaldehydes from furfural and anilines^{27,28}. Lewis and Mulquiney³⁰⁻³² have extensively studied the reaction of aryl amines and furan-2-carbaldehyde and have identified the formation of the intermediate “Stenhouse salt” (**Scheme-II**).

Which under the acid or basic conditions leads to the formation of various products: 1-aryl-3-hydroxypyrrole and 1-arylpyrrole-2-carbaldehydes.

FTIR analysis: Assignment of selected characteristics IR bands provides significant indication for the formation of diaryl pyrrole-2-carbaldehydes. The aldehydic group (C=O) and (C-H) absorbed in the expected region; (C=O) in the 1610-1681 cm^{-1} , (C-H) stretch of aldehydes show a weak band around 2846-2863 cm^{-1} , while NO_2 group present in some compounds

Scheme-I

Mechanism:

Scheme-II

shows characteristics strong band in 1341-1298 and at 1600-1584 cm^{-1} region.

¹H NMR analysis: The ¹H NMR spectra (300 MHz, CDCl_3) of the starting aryl furfurals and diaryl pyrrole-2-aldehydes show characteristic signals between 9.64-9.72 ppm for aldehydic proton and two doublet at 6.78-6.98 and 7.29-7.96 ppm for the pyrrole ring hydrogens.

¹³C NMR analysis: Finally, ¹³C NMR (75 MHz, CDCl_3) spectra of all compounds were recorded and spectral signals are in good agreement with the structures. Carbon of $\text{C}=\text{O}$ displayed signals at 177.21-177.72 ppm in the arylfuran-2-carbaldehydes and diarylpyrrole-2-carbaldehydes while pyrrole ring carbons show signals for their characteristic positions.

Mass spectra: Mass spectra of all compounds were recorded and their values are given in the experimental section. These characterize the formation of starting arylfuran-2-carbaldehydes and diarylpyrrole-2-carbaldehydes. All the new compounds displayed expected molecular ion peaks.

Conclusion

A good and efficient method for the preparation of diarylpyrrole-2-carbaldehydes by the ring transformation of arylfuran-2-carbaldehydes in acidic media is presented in this paper. From these diaryl pyrrole-2-carbaldehydes, various other heterocyclic compounds can be synthesized. Further work is in progress.

ACKNOWLEDGEMENTS

The authors (SA and AN) acknowledged the financial support by HEC, Govt. of Pakistan in the form of an indigenous PhD fellowship.

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